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(54) A method of forming coatings

(57) A coating is formed on a substrate by depositing a solution comprising a resin containing at least 2 Si-H groups and a solvent in a manner in which at least 5 volume % of the solvent remains in the coating after deposition followed by exposing the coating to an envi-

ronment comprising a basic catalyst and water at a concentration sufficient to cause condensation of the Si-H groups and evaporating the solvent from the coating to form a porous network coating. The method of the invention is particularly useful for applying low dielectric constant coatings on electronic devices.

PCT, (AP) for 1

coat → porous film
no solvent residue

Catalyst + H₂O
Hydrosilyl
Condense
Cure
Siloxane bonds

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of, polycarbonates, acrylics, polyesters, ceramics, leather, textiles and metals.

[0015] As used in the present invention the expression "ceramic" includes ceramics such as amorphous silica and ceramic-like materials such as amorphous silica-like materials that are not fully free of carbon and/or hydrogen but are otherwise ceramic in character and the expressions "electronic device" or "electronic circuit" include, but are not limited to, silicon based devices, gallium arsenide based devices, silicon carbide based devices, focal plane arrays, optoelectronic devices, photovoltaic cells and optical devices.

[0016] The resins containing at least 2 Si-H groups useful in the present invention are not particularly limited so long as the Si-H bonds can be hydrolyzed and at least partially condensed by the basic catalyst and water to form a crosslinked network which serves as the structure for the porous network. Generally, such materials have the formula:

(R₃SiO_{1/2})_a(R₂SiO_{2/2})_b(RSiO_{3/2})_c(SiO_{4/2})_d wherein each R is independently selected from hydrogen, alkyl, alkenyl or aryl groups or alkyl, alkenyl or aryl groups substituted with a hetero atom such as a halogen, nitrogen, sulfur, oxygen or silicon and a, b, c and d are mole fractions of the particular unit and the their total is 1, with the proviso that at least 2 R groups per molecule are hydrogen and the material is sufficiently resinous in structure to form the desired network. Examples of alkyl groups are methyl, ethyl, propyl and butyl, with alkyls of 1-6 carbon atoms preferred. Examples of alkenyl groups include vinyl, allyl and hexenyl. Examples of aryls include phenyl. Examples of substituted groups include CF₃(CF₂)_nCH₂CH₂, (where n = 0-6).

[0017] Particularly preferred in the present invention are various hydridosiloxane resins, known as hydrogen silsesquioxane resins, comprising units of the formula HSi(OH)_x(OR)_yO_{z/2}. In this formula, each R is as defined above. When these R groups are bonded to silicon through the oxygen atom, they form a hydrolyzable substituent. In the above formula, x = 0 to 2; y = 0 to 2; z = 1 to 3 and x + y + z = 3. These resins may be essentially fully condensed (HSiO_{3/2})_n where n is 8 or greater or they may be only partially hydrolyzed (i.e., containing some Si-OR) and/or partially condensed (i.e., containing some Si-OH).

[0018] The structure of the resin is not specifically limited. The structure of the resin may be what is generally known at ladder-type, cage-type or mixtures thereof. The resins may contain endgroups such as hydroxyl groups, triorganosiloxy groups, diorganohydrogensiloxy groups, trialkoxysiloxy groups and dialkoxysiloxy groups. Although not represented by the structure, the resins may also contain a small number (e.g. less than about 10%) of the silicon atoms which have either 0 or 2 hydrogen atoms attached thereto and/or a small number of SiC groups such as CH₃SiO_{3/2} or HCH₃SiO_{2/2} groups.

[0019] The above resins containing at least 2 Si-H groups and method for their production are known by U.S. Patent 3,615,272 which teaches the production of an essentially fully condensed hydrogen silsesquioxane resin (which may contain up to 100-300 ppm silanol) by a process comprising hydrolyzing trichlorosilane in a benzenesulfonic acid hydrate hydrolysis medium and then washing the resultant resin with water or aqueous sulfuric acid. Similarly, in U.S. Patent 5,010,159 teaches a method comprising hydrolyzing hydridosilanes in an arylsulfonic acid hydrate hydrolysis medium to form a resin which is then contacted with a neutralizing agent.

[0020] Other hydridosiloxane resins, such as those described by U.S. Patent 4,999,397; those described by U.S. Patent 5,210,160; those produced by hydrolyzing an alkoxy or acyloxy silane in an acidic, alcoholic hydrolysis medium; those described in Kokai Patent Nos. 59-178749, 60-86017 and 63-107122; or any other equivalent hydridosiloxane, will also function herein.

[0021] In a preferred embodiment of the invention, specific molecular weight fractions of the above hydrogen silsesquioxane resins may also be used in this process. Such fractions and methods for their preparation are taught in U.S. Patents 5,063,267 and 5,416,190. A preferred fraction comprises material wherein at least 75% of the polymeric species have a molecular weight above 1200 and a more preferred fraction comprises material wherein at least 75% of the polymeric species have a number average molecular weight between 1200 and 100,000.

[0022] The hydrogen silsesquioxane resin may contain other components so long as these components do not interfere with the integrity of the coating. It should be noted, however, that certain materials may increase the dielectric constant of the coating. Known additives include catalysts such as platinum, rhodium or copper catalyst which increase the rate and/or extent of cure of the resin as described in U.S. Patent 4,822,697.

[0023] Ceramic oxide precursors may also be used in combination with the hydrogen silsesquioxane resin. The ceramic oxide precursors useful herein include compounds of various metals such as aluminum, titanium, zirconium, tantalum, niobium and/or vanadium as well as various non-metallic compounds such as those of boron or phosphorous which may be dissolved in solution, hydrolyzed and subsequently pyrolyzed at relatively low temperature to form ceramic oxides. Ceramic oxide precursors useful herein are described in U.S. Patents 4,808,653, 5,008,320 and 5,290,394.

[0024] The above Si-H containing resins are applied to the substrates as solvent dispersions. Solvents which may be used include any agent or mixture of agents which will dissolve or disperse the resin to form a homogeneous liquid mixture without affecting the resulting coating or the substrate. These solvents can include alcohols such as ethyl alcohol or isopropyl alcohol; aromatic hydrocarbons such as benzene or toluene; branched or linear alkanes such as n-heptane, dodecane or nonane; branched or linear alkenes such as n-heptane, dodecene or tetradecene; ketones

- [0034] Contact of the coating with the basic catalyst and water can be accomplished by any means practical or desirable. For instance, the coating can be contacted with vapors of the basic catalyst and water vapor. Alternatively, the coating can be contacted with the basic catalyst and water in the liquid state. For instance the coating can be immersed in a basic catalyst solution containing water.
- 5 [0035] In a preferred embodiment of this invention, the resin coating is exposed to an environment comprising the basic catalyst and water in their vapor state. Exposure to the above conditions can be by any practical means. In a more preferred embodiment, the resin coating is exposed to ammonia and water vapor.
- 10 [0036] In this preferred embodiment, the coated substrate may, for instance, simply be placed in a container and the appropriate environment introduced therein or, alternatively, a stream of the basic catalyst and water may simply be directed at the coating.
- 15 [0037] The method used to generate the basic catalyst and water environment in this preferred embodiment is also generally not significant. Methods such as bubbling the basic catalyst (e.g., ammonia gas) through water or ammonium hydroxide solutions (to control the amount of water vapor present), heating a basic catalyst and water or heating water and introducing the basic catalyst gas (e.g., ammonia gas) are all functional herein. It is also contemplated that methods which generate basic catalyst vapors in situ such as the addition of water to amine salts or the addition of water to a silazane such as hexamethyldisilazane will also be effective.
- 20 [0038] The basic catalyst used in this preferred embodiment may be at any concentration desired. For example, the concentration may be from 0.01 up to a saturated atmosphere.
- 25 [0039] The exposure in this preferred embodiment of the invention can be at any temperature desired from room temperature up to 300°C. Generally, the temperature is in the range of from 20 up to 200°C. is preferred with a range of from 20 up to 100°C. being preferred.
- 30 [0040] The resin coating should be exposed to the basic catalyst and water environment in this preferred embodiment of the invention for the time necessary to hydrolyze the Si-H groups to form silanols (Si-OH) and for the silanols to at least partially condense to form Si-O-Si bonds. Generally, exposures of up to 20 minutes are preferred, with exposures of at least 1 second up to 5 minutes being more preferred. It should be noted that if the coatings of the invention are to be used as a dielectric layer, it is generally preferred to have a shorter exposure as longer exposures tend to increase the dielectric constant of the coating.
- 35 [0041] In an alternative embodiment of the invention, the coating is exposed to basic catalyst and then water in a liquid state. In a more preferred embodiment, the liquid basic catalyst and water is an ammonium hydroxide solution.
- 40 [0042] In this embodiment, the basic catalyst and water exposure is usually conducted by merely immersing the coated substrate in a solution. Other equivalent methods, however, such as continuously flushing the coating with a basic catalyst and water solution would function as well. In addition, vacuum infiltration may also be used to increase penetration of the basic catalyst and water into the coating.
- 45 [0043] The basic catalyst solution used in this embodiment may be at any concentration desired. Generally, when ammonium hydroxide is used, a concentrated aqueous solution (28-30%) is preferred since the duration of exposure is thereby shortened. When dilute solutions are to be used, the diluent is generally water.
- 50 [0044] Exposure to the basic catalyst and water solution in this embodiment may be conducted at any temperature and atmospheric pressure desired. Temperatures of from room temperature (20-30°C.) up to the boiling point of the basic catalyst solution and atmospheres from below to above atmospheric pressure are all contemplated herein. From a practical standpoint, however, it is preferred that the exposure occur at room temperature and at atmospheric pressure.
- 55 [0045] The resin coating is exposed to the basic catalyst solution in this embodiment of the invention for the time necessary to hydrolyze the Si-H groups to form silanols (Si-OH) and for the silanols to at least partially condense to form Si-O-Si bonds. Generally, exposures of up to 2 hours are preferred, with exposures of at least 1 second up to 15 minutes being more preferred.
- 60 [0046] In another alternative embodiment of this invention, the coating is exposed to both a liquid basic catalyst and water environment (e.g., ammonium hydroxide) and a gaseous basic catalyst and water vapor environments (ammonia gas and water vapor). The exposures in this embodiment of the invention may be either sequential or concomitant and are generally under the same conditions as those described above.
- 65 [0047] After the resin coating is exposed to one of the above environments, the solvent is then removed from the coating. This can be accomplished by any desired means. For instance, the coating can be heated to complete the condensation of silanols formed.
- 70 [0048] If desired, the resultant coating is subjected to a temperature converting the coating to a ceramic before, during or after solvent removal. Generally, this temperature is above room temperature with a range of from 50°C. to 500°C. being preferred. Higher temperatures usually result in quicker and more complete conversion to a ceramic, but these temperatures also may have detrimental effects on various temperature sensitive substrates. The coatings are usually subjected to these temperatures for a time sufficient to ceramify the coating, generally up to 6 hours, with a range of between 5 minutes and 6 hours being preferred, and a range of between 10 minutes and 2 hours being more

EXAMPLE 2

[0058] H-resin, prepared by the method of US Patent 3,615,272, was diluted to 26 weight percent solids in methyl-isobutylketone. The H-Resin/methylisobutylketone solution was diluted with 30 parts per hundred or 23 weight percent tetradecone. Two 4 inch diameter 1 mOhm-cm, n-type, silicon wafers were coated with the solution by spinning at 3000 rpm's for 20 seconds. One of the wafers was than exposed to an ammonia atmosphere with ambient moisture for 30 seconds and than heated for 10 minutes in nitrogen at 450°C. The dielectric constant of the film on the wafer was determined to be 1.71. The second wafer was used as a comparative example. It was placed in a vacuum oven at 80°C. for 10 minutes to remove the remaining tetradecone solvent in the film. After solvent removal, the wafer was exposed to an ammonia atmosphere with ambient moisture for 30 seconds and than heated for 10 minutes in nitrogen at 450°C. The dielectric constant of the second wafer was determined to be 2.97.

EXAMPLE 3

[0059] H-resin, prepared by the method of US Patent 3,615,272, was diluted to 26 weight percent solids in methyl-isobutylketone. The H-Resin/methylisobutylketone solution was diluted with different high boiling point solvents to form the series of solutions listed in Table 3. 4 inch diameter 1 mOhm-cm, n-type, silicon wafers were coated with each of the solutions listed in Table 3 by spinning at 3000 rpm's for 20 seconds.

[0060] The coated silicon wafers were exposed to an ammonia atmosphere with ambient moisture for 30 seconds and then heated for 10 minutes in nitrogen at 450°C. Table 4 shows the effect of various boiling point solvents on the resulting dielectric constant of the films.

Table 3

Solution Number	Solvent (Weight %)	Boiling Point
1	100% MIBK	117.4
2	propylene glycol methyl ether (16.6%)	120
3	propylene glycol n-butyl ether (16.6%)	171
4	tetradecone (16.6%)	254

Table 4

Solution Number	Dielectric Constant
1	3.0
2	3.3
3	3.2
4	1.91

EXAMPLE 4

[0061] H-resin, prepared by the method of US Patent 3,615,272, was diluted with methylisobutylketone or octamethyltetrasiloxane, as listed in Table 5, to the concentration listed in Table 5. The H-Resin/methylisobutylketone or siloxane solution was then diluted with tetradecone in the amount listed in Table 5. 4 inch diameter 1 mOhm-cm, n-type, silicon wafers were coated with each of the solutions listed in Table 5 by spinning at the speed and for the time listed in Table 5.

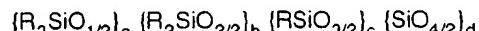
[0062] The coated silicon wafers were exposed to an ammonia atmosphere with ambient moisture for the time indicated in Table 5 and then heated for 10 minutes in nitrogen at 450°C. Table 6 shows the effect of various boiling point solvents on the resulting dielectric constant of the films.

Claims

1. A method of forming a coating on a substrate comprising:

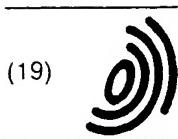
5 depositing a coating on a substrate with a solution comprising a resin containing at least 2 Si-H groups and a solvent in a manner in which at least 5 volume % of the solvent remains in the coating after deposition; exposing the coating to an environment comprising a basic catalyst and water at a concentration to cause hydrolysis of the Si-H groups and at least partial condensation; and evaporating the solvent from the coating to form a porous network coating.

- 10 2. The method of claim 1 wherein the porous network coating is heated to a temperature to convert the coating to a ceramic.
- 15 3. The method of claim 1 or 2, wherein the resin containing at least 2 Si-H groups has the formula:



20 wherein each R is independently selected from hydrogen, alkyl, alkenyl and aryl groups and alkyl, alkenyl and aryl groups substituted with halogen, nitrogen, oxygen, sulfur or silicon atoms, with the proviso that at least 2 R groups are hydrogen.

- 25 4. The method of claim 3 wherein the resin comprises hydrogen silsesquioxane resin of the structure selected from $(HSiO_{3/2})_n$, a polymer having units of the formula $HSi(OH)_aO_{3-x}2$ or a polymer having units of the formula $HSi(OH)_x(OR)_yO_{2/2}$, wherein each R is independently an organic group which, when bonded to silicon through the oxygen atom, forms a hydrolyzable substituent, a = 0-2, x = 0-2, y = 0-2, z = 1-3, x + y + z = 3, n is an integer greater than 3 and the average value of y over all of the units of the polymer is greater than 0.
- 30 5. The method according to any of claims 1 to 4, wherein the solvent is selected from alcohols, aromatic hydrocarbons, alkanes, alkenes, ketones, esters, ethers or mixtures thereof and is present in an amount sufficient to dissolve the hydrogen silsesquioxane to between 0.1 and 95 weight percent.
- 35 6. The method of claim 5, wherein the solvent has a boiling point greater than 175°C.
7. The method of claim 5, wherein the solvent is a mixture of solvents and at least one of the solvents has a boiling point greater than 175°C.
- 40 8. The method of claim 6 or 7, wherein the solvent with a boiling point greater than 175°C. is a hydrocarbon.
9. The method according to any of claims 2 to 8, wherein the coating is heated to a temperature of 50 to 500°C. for up to 6 hours.
- 45 10. The method according to any of claims 1 to 9, wherein the substrate is coated in a closed system to inhibit evaporation of the solvent.
11. The method according to any of claims 1 to 10, wherein the coating is exposed to ammonia and water vapors for up to 4 hours at a temperature of between 20°C. and 300°C.
- 50 12. The method according to any of claims 1 to 11, in which the formed porous network coating has a dielectric constant of 1.1 to 2.4.
13. The method of claim 12, in which the formed porous network coating has a dielectric constant of 1.5 to 2.2.
- 55 14. An electronic device containing a coating prepared by the method according to any of claims 1 to 13.
15. An electronic circuit containing a coating prepared by the method according to any of claims 1 to 14.



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ronment comprising a basic catalyst and water at a concentration sufficient to cause condensation of the Si-H groups and evaporating the solvent from the coating to form a porous network coating. The method of the invention is particularly useful for applying low dielectric constant coatings on electronic devices.

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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